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TITANIUM ALLOYED WITH BORON (POSTPRINT)

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14. ABSTRACT
Titanium alloys offer attractive mechanical and physical property combinations, with make them desirable for a variety of critical applications. Titanium alloys are proved to be reliable materials for important aerospace applications including many engine and airframe components, and the applications are expanding further in the next generation aircraft. The cost of titanium is still a major factor in the selection of titanium. A majority of the cost of titanium is associated with processing which is essential to obtain controlled microstructures. Small additions of boron to conventional titanium alloys have been found to produce significant changes to the microstructures and associated properties. Grain refinement and improved strength and stiffness are first-order effects, which lead to possibilities for developing novel and affordable processing methodologies and to enhance performance over conventional titanium alloys. Ongoing efforts to develop affordable titanium technologies for potential aerospace applications will be discussed in this paper.

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TITANIUM ALLOYED WITH BORON

Trace boron additions refine the cast grain size of conventional titanium alloys by roughly an order magnitude.

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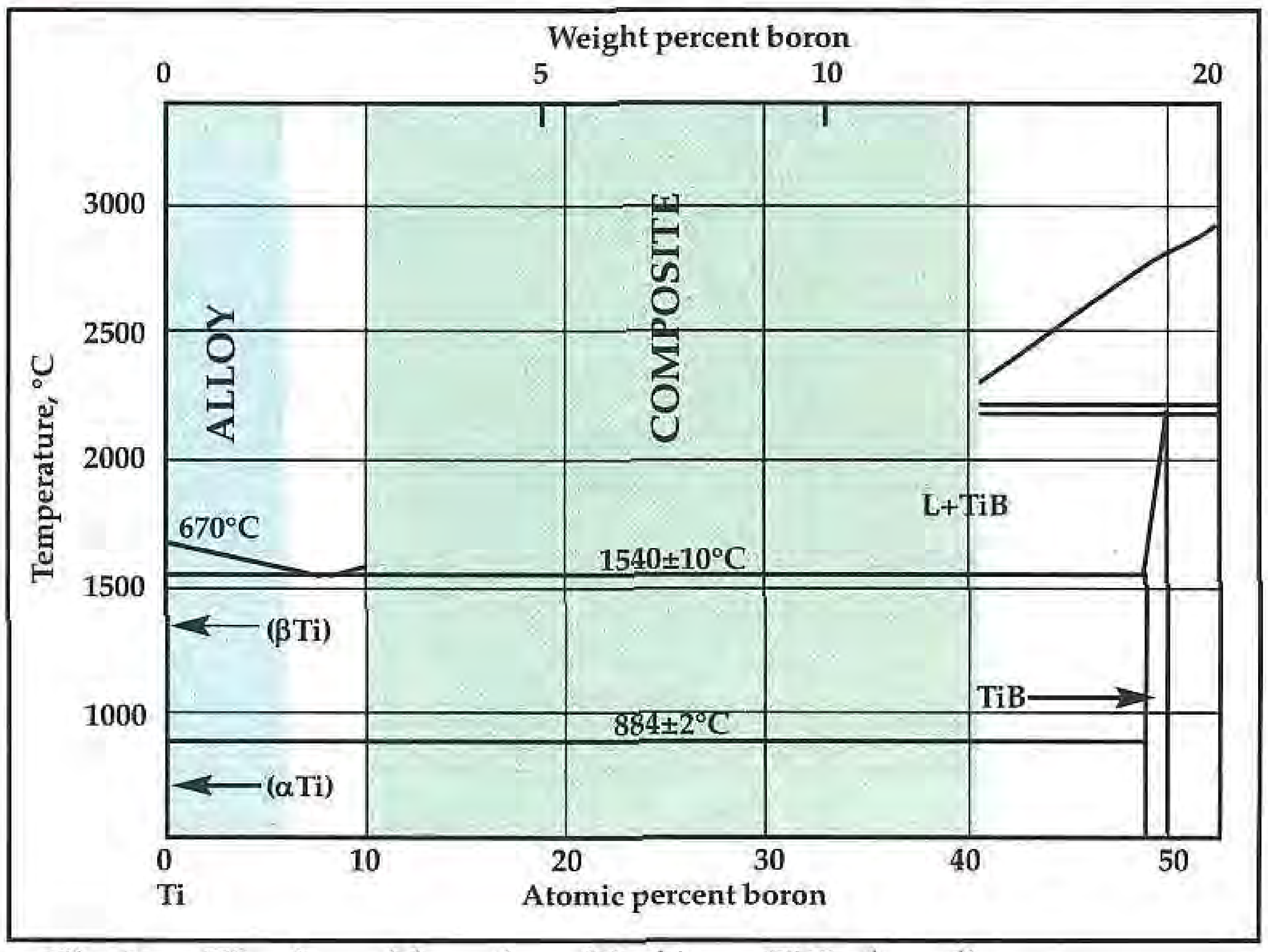

Fig. 1 — Titanium-rich section of the binary Ti-B phase diagram.

Small additions of boron to conventional titanium alloys have been found to produce significant changes to the microstructures and associated properties. Grain refinement and improved strength and stiffness are first-order effects, which lead to possibilities for developing novel and affordable processing methodologies and to enhance performance over conventional titanium alloys. In this article, we introduce this new class of titanium alloys and describe unique formability benefits achieved via engineering microstructures.

Ti-B material system

Boron is completely soluble in the liquid phase of titanium, but is essentially insoluble in the solid titanium phases (high temperature beta or room temperature alpha). Negligible solid solubility of boron in titanium eliminates the embrittlement problem commonly caused by other interstitial elements such as hydrogen, carbon, or oxygen. The Ti-rich end of the binary Ti-B phase diagram is shown in Fig. 1.

The boron added to titanium precipitates in the form of intermetallic TiB phase for additions below about 14 wt.% (40 at.%). TiB forms via the eutectic reaction L→ β +TiB, with the binary eutectic composition of 2 wt% B.

The TiB phase offers unique advantages. The density of TiB is comparable to that of titanium, but the stiffness is about five times higher. Therefore, the TiB phase provides significant increases in strength and stiffness without increasing density. TiB also has excellent crystallographic compatibility with titanium, providing atomically sharp interfaces and chemical compatibility. The coefficient of thermal expansion of TiB is comparable to that of titanium, which eliminates residual stresses at the interfaces.

The crystal structure of TiB is orthorhombic, and particles grow as short whiskers about one micron in diameter and ten microns long that are efficient strengtheners below the eutectic limit (1.55 wt.%B for the most widely used titanium alloy Ti-6Al-4V). Hypoeutectic alloys have microstructures, processing, and property combinations similar to alloys without boron. Therefore, Ti-B materials can be considered as boron-modified titanium alloys at boron levels below the eutectic limit.

Above the eutectic, the TiB phase is in equilibrium with the liquid, and it grows rapidly, leading to the formation of coarse (>100 microns) primary TiB particles. Although the higher volume fraction of TiB significantly increases stiffness, strength, and wear resistance, the fracture behavior changes from ductile to brittle, and this results in a significant debit in damage tolerance. The microstructures and properties of hypereutectic Ti-B compositions are best classified as discontinuously reinforced titanium metal-matrix composites.

A value of 7% tensile elongation is often required by structural designers for fracture-critical applications. Ti-B alloys with low-to-

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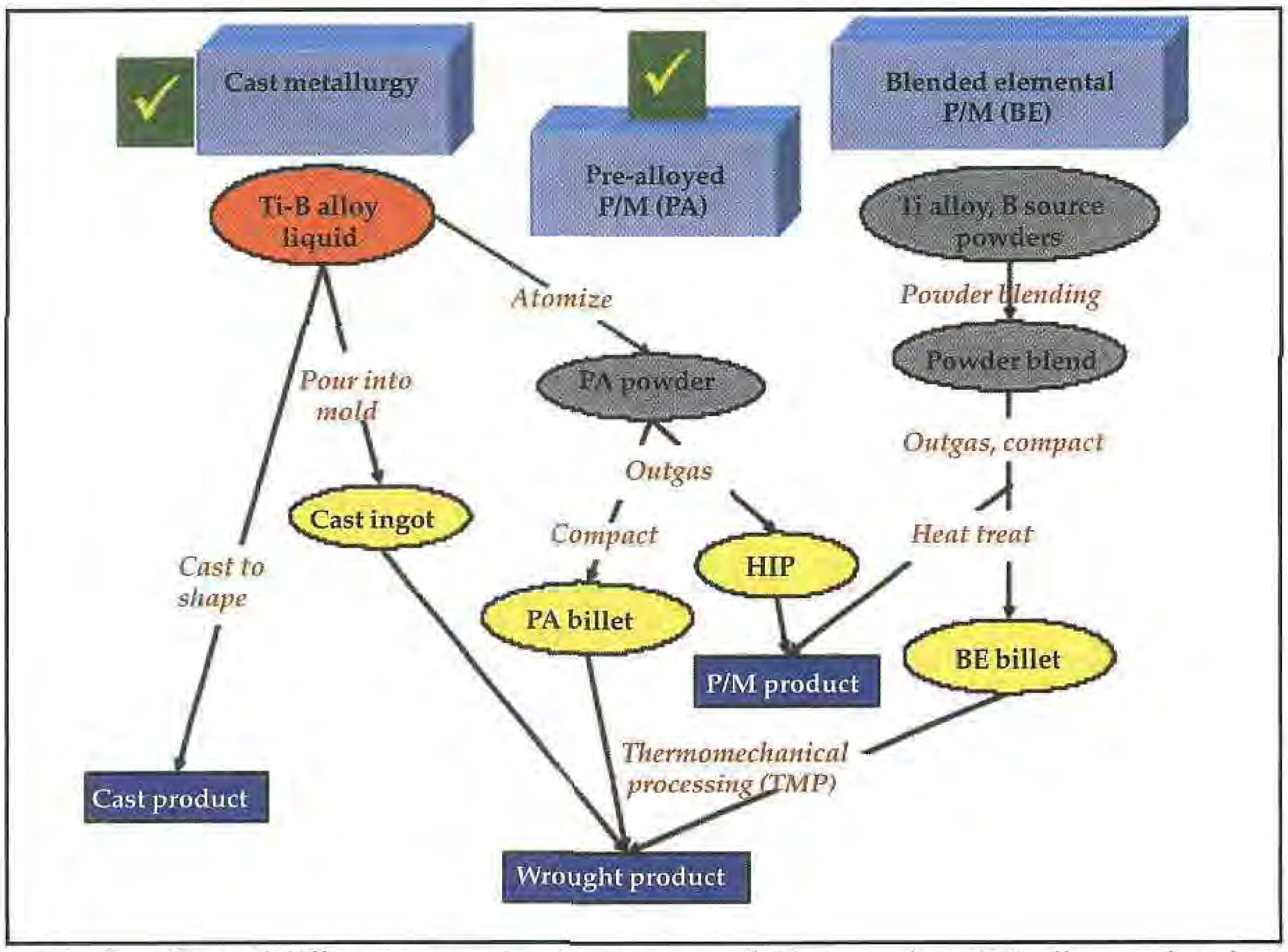

Fig. 2 — Several different processing routes are available to produce Ti-B alloys and various techniques can fabricate product forms.

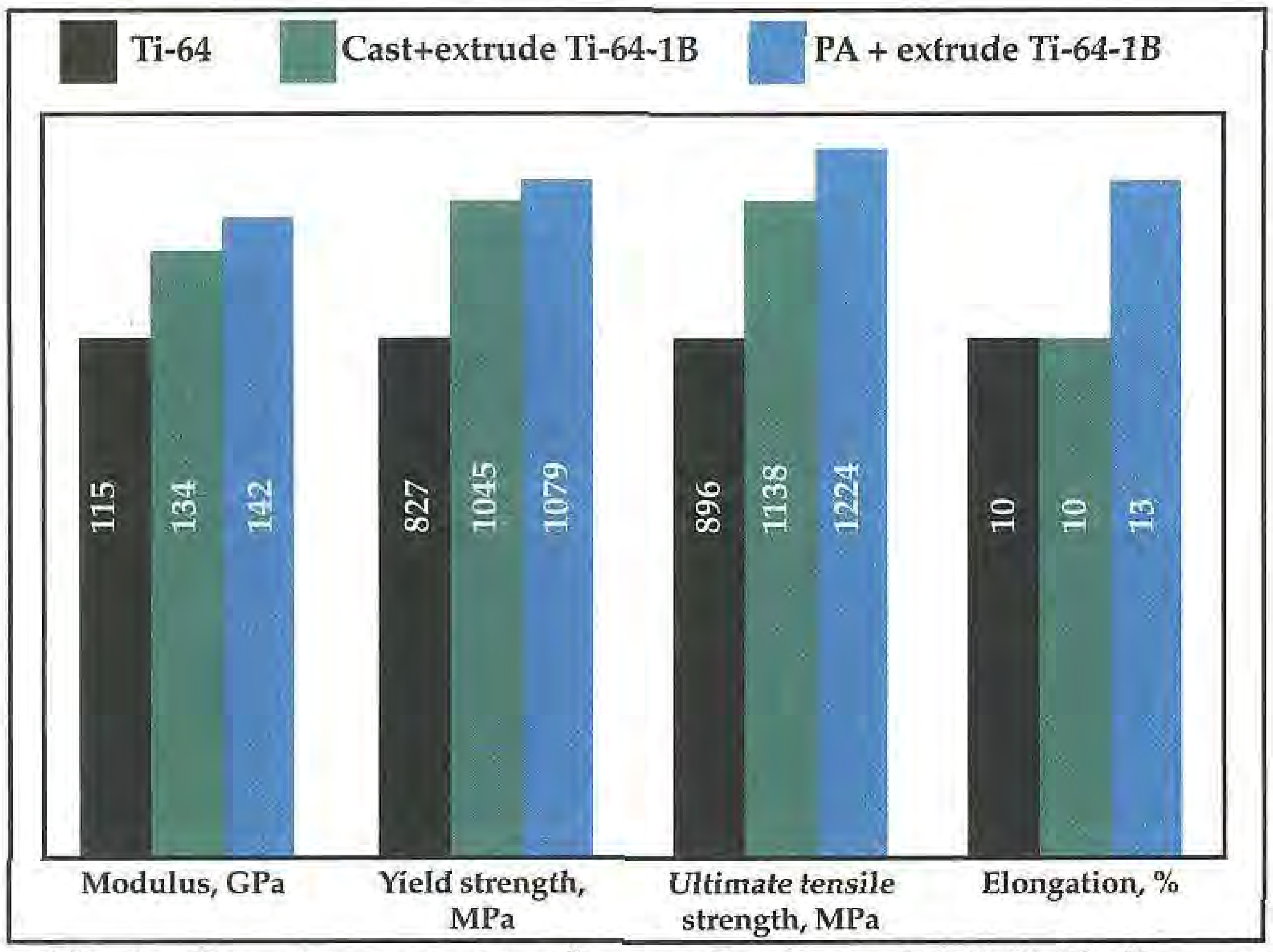

Fig. 3 — Room temperature tensile properties of extruded Ti-64-1B alloys produced via cast and powder metallurgy approaches.

modest boron concentrations (<1 wt.%) satisfy this requirement. These are relevant to aerospace applications, and we focus on these alloys in this article.

Ti-B alloys can be produced via traditional processing techniques such as liquid metallurgy and powder metallurgy. Various Ti-B alloy processing routes and product forms are illustrated in Fig. 2.

Casting titanium

In the conventional cast metallurgy approach, a boron source (e.g. TiB_2, elemental B, AlB_{12}) is added to the titanium alloy charge mix. Whatever the boron source, it completely dissolves and forms a Ti-B alloy melt. Additional titanium is added to compensate for the titanium scavenged from the alloy to transform the boron source to TiB. The liquid Ti-B melt can be directly poured into a shaped mold by conventional casting techniques to produce a Ti-B alloy casting, or into an ingot mold to produce a Ti-B alloy cast ingot. The cast ingot can be subjected to conventional thermomechanical processing (TMP) such as forging, rolling, or extrusion to produce a wrought product.

Powder metal processing

Alternatively, the Ti-B alloy melt can be subjected to rapid solidification to produce pre-alloyed (PA) Ti-B powder via conventional powder-making processes (e.g. inert gas atomization). The TiB phase that forms in the solid state is uniformly distributed in each powder particle. PA powder can be outgassed (to remove any volatile impurities) and compacted by techniques such as hot isostatic pressing (HIP), which is common for Ti alloys to produce near-net shape products. The PA powder can also be compacted to billet preforms and subjected to TMP to manufacture wrought products.

Isotropic properties develop when TiB whiskers are randomly oriented. However, intentional alignment of the TiB whiskers through processes such as extrusion or rolling can further increase the properties along the direction of alignment.

The PA approach has the advantage of producing finer length-scale microstructural features due to shorter times for growth during rapid solidification. In addition, the PA approach also offers the advantage of producing supersaturated boron due to non-equilibrium cooling conditions. The supersaturated boron can be forced out in a controlled fashion via subsequent thermal exposure in the solid state to form nanometer-sized TiB precipitates that could provide additional strengthening and improve isotropy. Both cast and PA approaches are limited to hypoeutectic compositions due to the formation of coarse primary TiB particles in hypereutectic compositions.

Room temperature tensile properties of Ti-64 modified with 1%B (Ti-64-1B) in the extruded condition produced via cast and PA approaches are presented in Fig. 3. Compared to Ti-64, addition of 1%B produces 20-30% improvements in tensile modulus and strength with no debit in ductility.

Blended elemental powder processing

Ti-B products can also be manufactured through a blended-elemental (BE) powder metallurgy process conducted completely in the solid state (Fig. 2). In the BE process, powders of Ti alloy and boron source are intermixed with an appropriate blending process (wet/dry). The powder blend is outgassed and consolidated to prepare a compact. The BE compact is then subjected to a reaction heat treatment to convert the boron source into TiB.

Like the PA process, the BE process can produce either near-net shapes via compaction, or net shapes via compaction plus TMP. The BE ap-

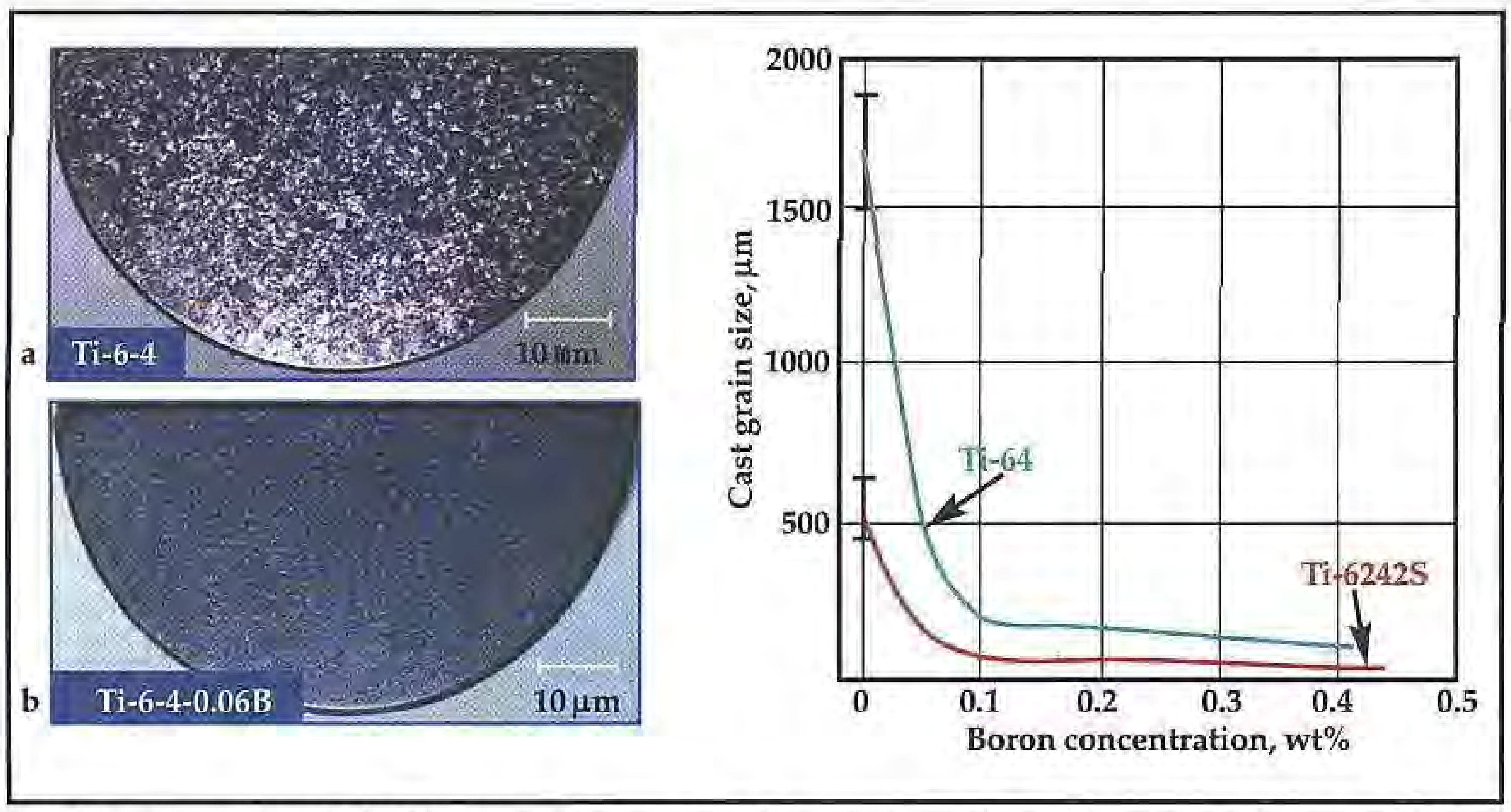

Fig. 4 — a) and b) illustrate the grain refinement produced by a trace boron addition. The graph shows the variation of grain size of Ti-64 and Ti-6242S alloys with boron concentration.

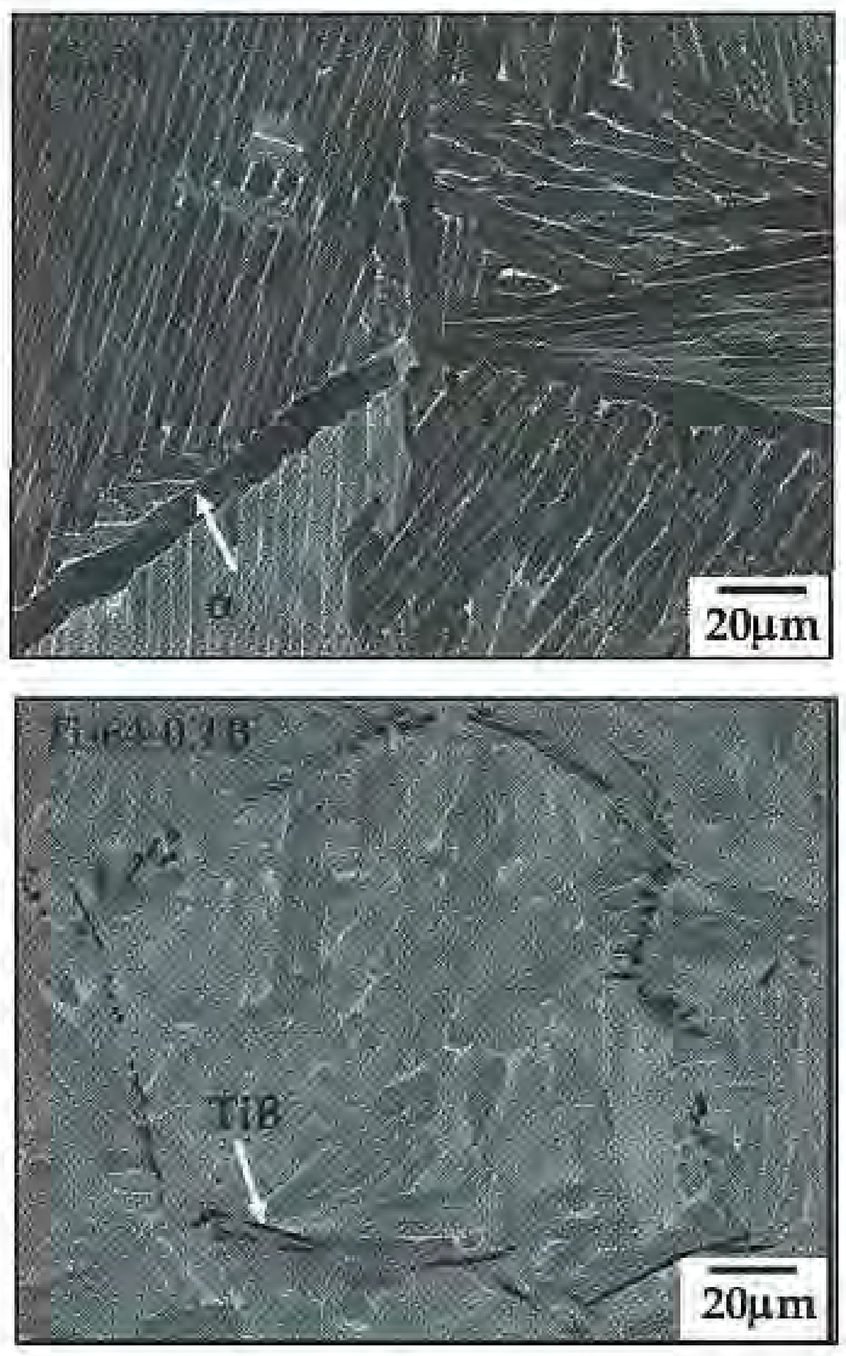

Fig. 5 — These backscattered electron images demonstrate how a trace boron addition reduces the thickness of the brittle grain boundary alpha phase.

proach offers the ability to introduce higher amounts of TiB without the formation of coarse primary TiB, since processing is conducted completely in the solid state and is well-suited for producing Ti-B composites. The BE process has been successful in producing several commercial products (e.g. automobile engine valves, sporting goods). However, the BE approach results in coarser microstructural features than other approaches due to high temperatures and long times required for TiB conversion, and limited options exist to control this reaction.

Grain refinement

Solidification is a dominant processing route for metallic materials, and grain refinement is of significant industrial importance. Fine grain size improves many mechanical properties, such as strength, ductility, and damage tolerance, and it enhances subsequent mechanical working. The addition of inoculants to many molten metal alloys (for example, trace B to Al alloys) is the most common commercial practice to achieve grain refinement, but no such grain refinement mechanism is available for titanium alloys.

The effect of trace boron additions to titanium alloys on grain refinement has been systematically evaluated, and the results are summarized in Fig. 4. Macrographs recorded on transverse sections of Ti-64 and Ti-64-0.06B ingots are shown in Fig. 4a and 4b, which illustrate the dramatic grain refinement produced by the trace boron addition.

The variation of grain size of Ti-64 and Ti-6242S alloys with boron concentration is shown in the graph in Fig. 4. The addition of 0.1% boron refines the grain size by an order of magnitude. The grain size vs. boron concentration curves show a knee in the range 0.06-0.1%B. This indicates that a critical level of boron is required for dramatic grain refinement, beyond which grain size is reduced by only a small additional amount.

Trace boron addition also improves workability by reducing the thickness of the brittle grain boundary alpha phase (Fig. 5). In addition, TiB forms a necklace structure at the lowest boron levels, which helps in restricting grain growth during subsequent heat treatment/TMP operations.

The refined microstructure and improved properties of cast Ti-B alloys may enable replacement of more expensive machined components from cast and wrought product with more affordable cast-to-shape components.

Process enhancement

Grain refinement via trace boron addition may provide the ability to reduce/eliminate TMP steps necessary to produce high-quality titanium products. For example, studies of the rolling response of conventional and boron-modified Ti-64 showed that the as-cast alloy without boron exhibited poor workability manifested in the form of severe edge and surface cracks that are attributed to coarse grain size. The as-cast alloy containing trace boron, on the other hand, could be successfully rolled without any cracks, and the rolled product exhibited good surface finish and properties. Similar observations have been made in forging and extrusion processes. Therefore, a small boron addition offers the advantage of eliminating expensive and time-consuming ingot breakdown and billet conditioning steps conventionally used to improve the workability.

Efforts are underway to take advantage of improved workability via small boron addition in the design of efficient TMP sequences with minimal process steps to reduce the processing cost and time associated with titanium products.

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References

[1] Marray JL, Liao PK, Spear KE: *Binary Alloy Phase Diagrams*, 1992, ASM International, Materials Park, Ohio, p.2.85.

[2] O.M. Ivasishin, Institute for Metal Physics, Kiev, Ukraine, private communication.

[3] Tamirisakandala S., Bhat R.B., Tiley J.S., Miracle D.B.:, Grain Refinement of Cast Titanium Alloys via Trace Boron Addition, *Scripta Mater.* 2005 53:1421-1426.